

Evaluation of Relationships Between Mainstream Smoke Acetaldehyde and “Tar” and Carbon Monoxide Yields in Tobacco Smoke and Reducing Sugars in Tobacco Blends of U.S. Commercial Cigarettes

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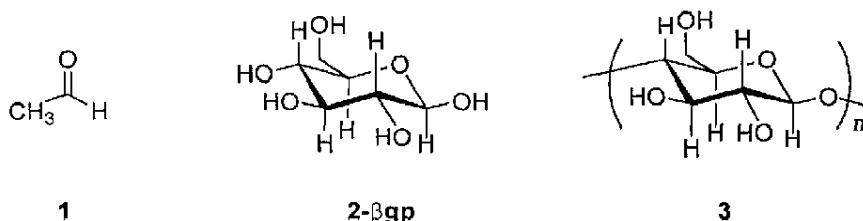
ABSTRACT

Mainstream smoke acetaldehyde, carbon monoxide and “tar” yields from a Philip Morris database of commercial cigarettes and reducing sugars in the tobacco blends were analyzed. MS smoke acetaldehyde is significantly correlated with “tar” yield and also with MS smoke carbon monoxide. The correlations found between MS smoke acetaldehyde yield and “tar” and MS smoke carbon monoxide support the conclusion that both acetaldehyde and carbon monoxide yields are affected more by cigarette design characteristics influencing total smoke production, such as filter ventilation, than by specific additives. MS smoke acetaldehyde yield is not correlated with reducing sugar concentration in tobacco blend. Over the time periods 1985-1988 and 1990-1993, for the available Philip Morris database of US commercial cigarettes, the concentration of reducing sugars either stayed the same or decreased slightly. The correlations and conclusions reported herein are consistent with the published literature, including the 1999 Massachusetts Benchmark Study.

INTRODUCTION

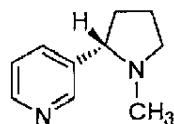
Acetaldehyde (**1**; sometime referred to as “AA” herein) has recently been classified as being a smoke component with significant potential biological activity.^{1,2} The US Consumer Products Safety Committee identified acetaldehyde as a cigarette smoke constituent of concern,³ and a study by the World Health Organization indicated that AA may be cytotoxic or genotoxic.² Two recent reports suggested that MS smoke acetaldehyde is derived from sugars added in tobacco processing^{4,5}. A recent review of

the scientific literature concluded that sugars, e.g., D-glucose (**2**, illustrated in its β -glucopyranose form **2- β gp**), do not lead to significant quantities of MS smoke acetaldehyde.⁶ This review further concluded that natural tobacco polysaccharides, e.g., cellulose (**3**), are likely to be the primary precursors of mainstream (MS) smoke acetaldehyde (**1**). In order to focus the development of potentially reduced-harm tobacco products and to address real scientific and technical issues, it is critical to identify accurately the source(s) of MS smoke acetaldehyde.



The purpose of this study is to analyze the available data on commercial cigarettes over a period of many years, which includes data on tobacco blend reducing sugars, MS smoke acetaldehyde yields and MS smoke carbon monoxide yields. We shall examine the hypothesis that sugars in tobacco lead to MS smoke acetaldehyde. We shall also examine if reducing sugar (RS) levels in tobacco blends of commercial cigarettes have increased for the years that complete and statistically meaningful data is available. By “complete and statistically meaningful data”, we mean having a large enough data set of commercial cigarettes for which measurements were made of the tobacco and/or smoke parameters of interest.

Nicotine (**4**) and “tar” yields have been measured and reported for US commercial cigarettes over the past decades. Measurement of MS smoke acetaldehyde yields have been reported only sporadically.⁷ There are two types of sugars in the tobacco blend; reducing sugars and non-reducing sugars. This distinction will be discussed in more detail below.



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Fortunately, the Philip Morris USA database contains data for both MS smoke acetaldehyde yield data and reducing sugars in the tobacco blend for a large number of US commercial cigarettes in the same time period. Limited data is available on carbon monoxide yields. The data originates from cigarettes sold in the United States in the years 1985-1988 and 1990-1993. All relevant data within the database was used in this work to examine the relationships between MS acetaldehyde yield and “tar” yields, carbon monoxide yields, and RS in tobacco.

The "1999 Massachusetts Benchmark Study" has recently become available.⁸ This collaborative effort of Brown & Williamson Tobacco Corporation, Lorillard Tobacco Company, Philip Morris, USA, and R. J. Reynolds Tobacco Company, is magnificent, in terms of the range of US commercial brands studied, the number of MS and sidestream (SS) smoke constituents quantified, the variety of analytical and statistical tools utilized, and the number of scientists and laboratories involved. MS smoke data was reported for acetaldehyde using a modified Massachusetts Benchmark Study (MBS) puff profile and FTC and MBS "tar, and FTC and MBS MS smoke carbon monoxide, among other smoke constituents. (A description of the various puff profiles is given in Table 1.) In 1997, Labstat Inc. produced a study of ten commercial US cigarettes in which MS smoke nicotine, "tar", and acetaldehyde smoke yields were reported.⁹ And most recently, Chepiga, et al. reported relevant smoke constituent yields for a set of 26 US commercial cigarettes.¹⁰

We herein report an evaluation of this data and observe (1) that MS smoke acetaldehyde is highly correlated with "tar" and, when measured, with MS smoke carbon monoxide for these different sets of US commercial cigarettes; and (2) neither MS smoke AA nor the ratio AA/"tar" is correlated with reducing sugars in the tobacco blend. The former observation supports an earlier conclusion⁷ that MS smoke AA yields reflect total smoke formation. The latter observation indicates that reducing sugars are not an important source of AA in MS smoke of commercial cigarettes. In addition, for the US commercial cigarettes for which data is available in the 1985-1993 time period, the levels of RS appears to have decreased.

METHODS OF COMPARING SMOKE YIELD DATA

In analyses of tobacco and MS smoke data, four types of relationships can be evaluated:

- Case (1): One tobacco constituent with a MS smoke constituent;
- Case (2): One MS smoke component with a second MS smoke constituent.
 - (a) One smoke constituent exists primarily in the gas phase, the second in the particulate phase.
 - (b) Both smoke constituents exist primarily in the same phase.

Consider Case 1. When examining the relationship between a tobacco constituent with a MS smoke constituent, one may have to normalize the smoke constituent to total smoke formation. For example, one might ask the question, "Does the addition of reducing sugars to tobacco caused an increase in MS smoke acetaldehyde?" One approach to answering this question would be to compare the MS smoke yields of acetaldehyde within a series of cigarettes containing levels of reducing sugars in the tobacco blend.

An important understanding must now be made. One must examine not just the variation in MS smoke acetaldehyde yield but rather the variation in acetaldehyde yield

relative to the yield of total smoke formation. "Total smoke formation" can be estimated by TPM, or "tar", or possibly "total gas phase yield," or even a surrogate for these parameters, e.g., nicotine yield for "tar" or carbon monoxide yield for "total gas phase yield".⁸ If the levels of MS smoke acetaldehyde do vary, for example, with the same multiplier as "tar" yield or carbon monoxide yield varied, then no "selective" variation of MS smoke acetaldehyde would have been found relative to RS in the tobacco.

In other words, one must demonstrate the finding of a "specific" or "selective" variation (increase or decrease) of a constituent's MS smoke yield compared to the MS smoke yield of all other relevant smoke constituents. If a "global" increase or decrease is observed upon the addition of a tobacco blend constituent, this may reflect an increase in total smoke formation. One cause for such a global variation could be a change in burn rate characteristics, increasing or decreasing puff count, increasing or decreasing ventilation, etc.

Consider Case 2. Since both parameters are smoke constituents, it is not necessary to normalize one or both constituents relative to "tar". In some specific instances, useful information can be obtained by considering, for example, the ratio "MS smoke component XYZ"/"tar" as a function of "tar" yield.

THE RELATIONSHIP BETWEEN MS SMOKE ACETALDEHYDE AND "TAR" AND MS SMOKE CARBON MONOXIDE

Acetaldehyde is a gas at room temperature and pressure (21 °C). A very reactive substance, acetaldehyde likely undergoes some degradation during trapping and during analysis and possibly prior to exiting the cigarette.¹¹ Table 2 compares acetaldehyde with nicotine in terms of some physical and smoke chemistry properties.

The AA and "tar" data from the Philip Morris database for 1985-1988 and 1990-1993 are summarized in Table 3. The data sets for these years were selected for our analysis on the basis that simultaneous measurements of the parameters of interest were made across a wide spectrum of commercial brands, representing a large sample of cigarettes in the marketplace. In some instances in this work, the data for one set of correlations derived from a collection of cigarette brands which was *not* identical to the cigarette brands for which data was available for another correlation. The available data for other years was limited either by restricted sampling of the marketplace or incomplete measurement of the parameters of interest.

The mean values of FTC MS smoke acetaldehyde are relatively constant from 1985 to 1993 (ca. 0.52 mg/cigarette). In all years, a wide range of yields is observed. Similarly, "tar" yields appear to be somewhat constant during the 1985 to 1993 period (ca. 10.8 mg).

Table 4 lists the MS smoke acetaldehyde and "tar" yields for US commercial cigarettes reported in three recent studies. In the Labstat study, "tar" was determined using three puff profiles (see Table 1) while AA was measured using only the FTC paradigm. In contrast, in the Massachusetts Benchmark Study, "tar" yields were measured using both the FTC and another puff profile, the MBS profile, while MS smoke

acetaldehyde yield was determined using only the MBS paradigm. The recent Chepiga, et al. work used the FTC puff profile. While these profiles are different, comparison of Tables 3 and 4 indicates a reasonable degree of consistency.

Of particular importance is the uniform observation of excellent correlations between MS smoke acetaldehyde and "tar." These are summarized in Tables 5-7.

Table 5 lists the statistics for the relationship between MS smoke acetaldehyde delivery vs. "tar" for the brands tested in the 1985-1988 and 1990-1993 time periods. Linear relationships are observed, though with a fair amount of scatter, as quantified by r^2 values from 0.70-0.87. Two representative correlations are shown in Figures 1-2 for 1985 and 1992, respectively. Throughout the time period studied, the slopes and intercepts of the lines appear to be very similar.

As shown in Table 6, the Massachusetts Benchmark Study reported two second order (quadratic equations) correlations, between MS smoke acetaldehyde with "tar" ($r^2 = 0.8209$) as well as with MS smoke carbon monoxide ($r^2 = 0.9257$). No explanation was provided for the use of a second order correlation model, except for the authors' notation that this is the form currently used by tobacco manufacturers in the United States in their report to the Commonwealth of Massachusetts which incorporates the so-called "Massachusetts nicotine multiplier".

In contrast, the Labstat data revealed either equivalent or superior correlations between MS smoke AA and "tar", compared with MS smoke AA and MS smoke carbon monoxide (see Table 7). The Labstat study contains data for three different puff profiles for "tar", but in one (FTC), "tar" yield for only eight of the ten cigarettes studied is reported. The Chepiga, et al. study obtained a superior correlation between MS AA yield and "tar" ($r^2 = 0.91$) using the FTC puff profile.

The Philip Morris database contained MS smoke acetaldehyde and carbon monoxide yields for the same cigarettes in only two years, 1985 and 1993 (116 and 117 brands for these years, respectively). A summary of the data is shown in Table 8. Carbon monoxide data is available for fewer brands than for "tar" and for MS smoke acetaldehyde, as seen by a comparison of the data in Table 3 with the data in Table 8. Excellent correlations are observed between MS smoke acetaldehyde and MS smoke carbon monoxide (Table 9), with $r^2 = 0.833$ and 0.934 for 1985 and 1993 data respectively. The correlation for 1993 is shown in Figure 3. These correlations are superior to those between MS smoke acetaldehyde and "tar" for the same years ($r^2 = 0.701$ and 0.832 for 1985 and 1993 data respectively; $n = 30$ and 135), though the cigarette brands included in the correlations are not the same. That acetaldehyde and CO correlate better than acetaldehyde and "tar" is consistent with the observations in the Massachusetts Benchmark study,⁸ though not with the more limited Labstat data set,⁹ and may well be related to the phase of the smoke constituent.

These four data sets represent smoke data for various sets and years of US commercial cigarettes. Taken together, the data clearly demonstrates that MS smoke acetaldehyde yields correlate significantly with indicators of total MS smoke formation, i.e., with both "tar" and carbon monoxide yields. These results suggest that AA

deliveries are affected more by cigarette design characteristics, e.g., ventilation and overall deliveries, than by specific tobacco blend constituents.

The superior correlations with carbon monoxide was attributed to the fact that acetaldehyde is primarily a gas phase constituent of MS smoke, as is carbon monoxide, while "tar" the sum of the particulate phase constituents, excluding nicotine and water.⁸ Many studies have shown that carbon monoxide in MS smoke is formed by a number of different types of processes, each undoubtedly representing numerous reactions.¹² These include thermal decomposition as well as combustion of tobacco materials as well as oxidation of carbon and reduction of carbon dioxide. Similarly, it is likely that MS smoke acetaldehyde is formed via numerous reaction pathways, from various tobacco constituents.

The ratio acetaldehyde/"tar" vs. "tar" is plotted in Figures 4-5 for 1985 and 1992, respectively, the same years used in Figures 1-2. Representative data for this ratio is also listed in Table 3. Because of the scatter observed in Figures 1-2, it follows that the acetaldehyde/"tar" v. "tar" points would likewise show scatter and this is the case. Perhaps the most interesting aspect of Figures 4-5 is the scatter at low "tar" values. Nonetheless, examination of a number of these relationships indicates that the ratio MS smoke acetaldehyde/"tar" is essentially independent of the "tar" yield.

Similarly, the ratio acetaldehyde/carbon monoxide vs. carbon monoxide is plotted in Figure 6 for 1985. A similar chart is obtained using the data for 1993. See data summary in Table 8. Examination of these two relationships suggests that the ratio MS smoke acetaldehyde/CO is essentially independent of the CO yield.

MS SMOKE ACETALDEHYDE YIELD AND REDUCING SUGARS IN TOBACCO

The hypothesis has been advanced that sugars added to the blends of commercial cigarettes increase the amount of acetaldehyde in MS smoke.^{4,13} Reducing sugars and non-reducing sugars are known tobacco additives.^{6,14,15} Table 10 shows the structures of the reducing sugars typically used in some commercial cigarettes. There is no simple analytical test for both reducing and non-reducing sugars. However, reducing sugars can be readily quantified by their known reaction with an oxidizing agent, e.g., Tollens' reagent. This well-known, effective and efficient analytical method transforms the aldehydic group (-CHO) in the sugar to a carboxylic acid, simultaneously converting, in a known molar ratio, silver ion to metallic silver. The metallic silver is then quantified. This is illustrated in Figure 7. The Tollens' reagent test for reducing sugars is often used as a surrogate for total sugars.

Total reducing sugars was quantified for many of the cigarettes in the Philip Morris database for which MS smoke acetaldehyde data is completely and extensively available (1985-1988 and 1990-1993). A summary of the data is shown in Table 11. There appears to be a modest decrease in reducing sugars from 8.1-8.7 % (on a dry weight basis) from the earlier years of this data set to 6.4-7.3 % in the 1988 to 1993 time period. This is graphically illustrated in Figure 8.

No correlation was observed between MS smoke acetaldehyde yield or the MS smoke acetaldehyde/"tar" ratio with reducing sugars. Significant scatter is observed in these relationships. Figure 9 illustrates a representative data set.

These results suggest that RS levels have not increased over the time period for which data is available. Further, the data indicates a lack of correlation between reducing sugar in the tobacco blend and MS smoke acetaldehyde yields. These conclusions are consistent with the literature and add further evidence to support the conclusion that sugars are not significant precursors to MS smoke acetaldehyde in commercial cigarettes.^{6,16}

I. CONCLUSIONS

The data, correlations, and conclusions reported herein are consistent with the available data and the published literature, including the recent outstanding 1999 Massachusetts Benchmark Study,⁸ the less comprehensive 1997 Labstat Report for the Commonwealth of Massachusetts,⁹ and other related studies.^{10,17,18} The following conclusions are based on all three studies and are consistent with other literature results.

1. MS smoke acetaldehyde is significantly correlated with "tar" yield and also with MS smoke carbon monoxide yield.
2. The correlations found between MS smoke acetaldehyde yield *and* "tar" and MS smoke carbon monoxide support the conclusion that both acetaldehyde and carbon monoxide yields are affected more by cigarette design characteristics influencing total smoke production, such as filter ventilation, than by specific additives.
3. MS acetaldehyde yield is not correlated with reducing sugar concentration in tobacco blend.
4. Over the time period 1985-1993, for the available Philip Morris database of US commercial cigarettes, the concentration of reducing sugars either stayed the same or decreased slightly.
5. We hypothesize that MS smoke yield for most constituents will be related to overall MS smoke delivery (gas phase or particulate phase), as measured by either total particulate matter (TPM) or "tar" or a specific gas phase component surrogate. For the latter, the Benchmark study proposed carbon monoxide.

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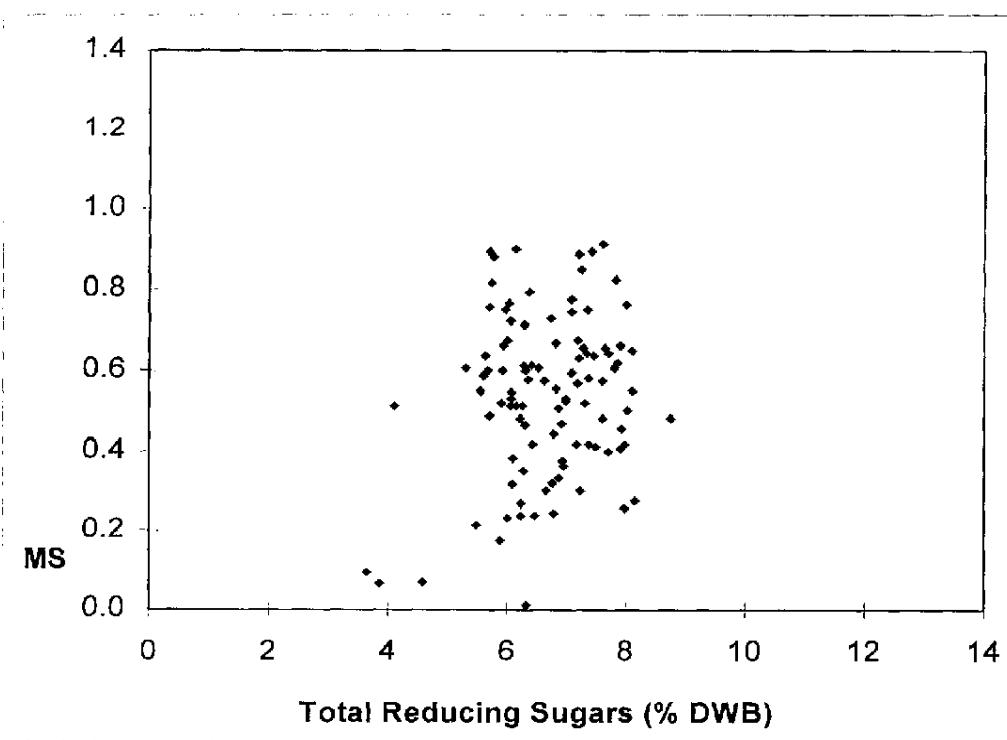


Figure 1. Plot of FTC MS smoke acetaldehyde vs. "tar" for 1985 (n = 135).

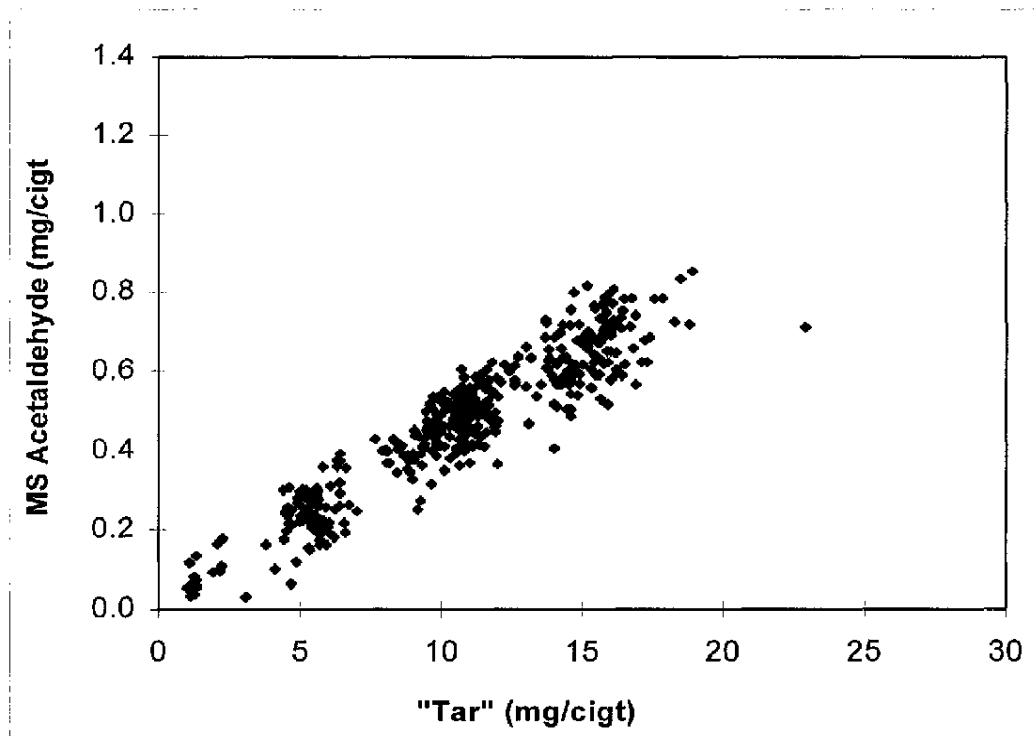


Figure 2. Plot of FTC MS smoke acetaldehyde vs. "tar" for 1992 (n = 422).

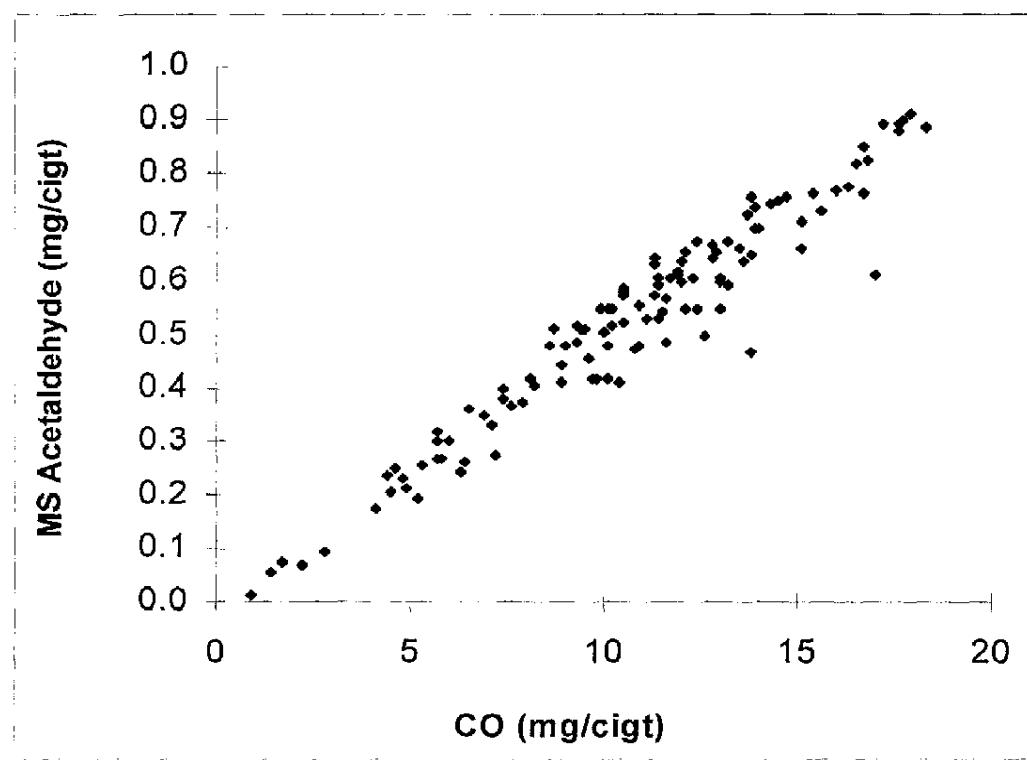


Figure 3. Plot of FTC MS smoke acetaldehyde vs. carbon monoxide for 1993 (n = 117).

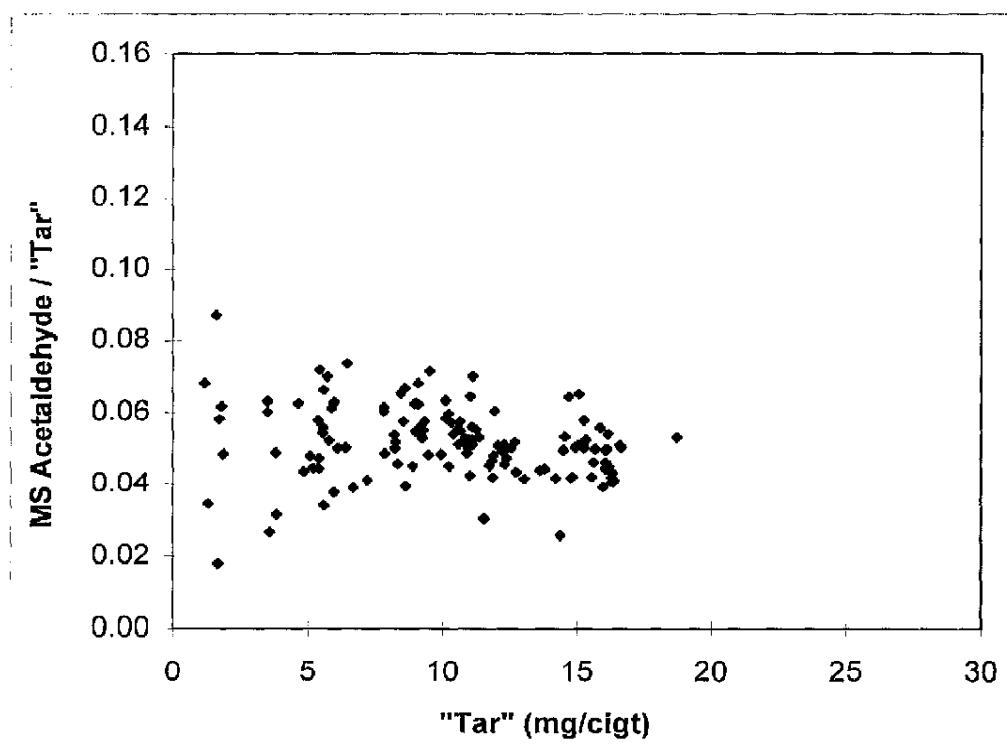


Figure 4. Plot of the ratio FTC MS acetaldehyde/"tar" vs. "tar" for 1985 ($n = 135$).

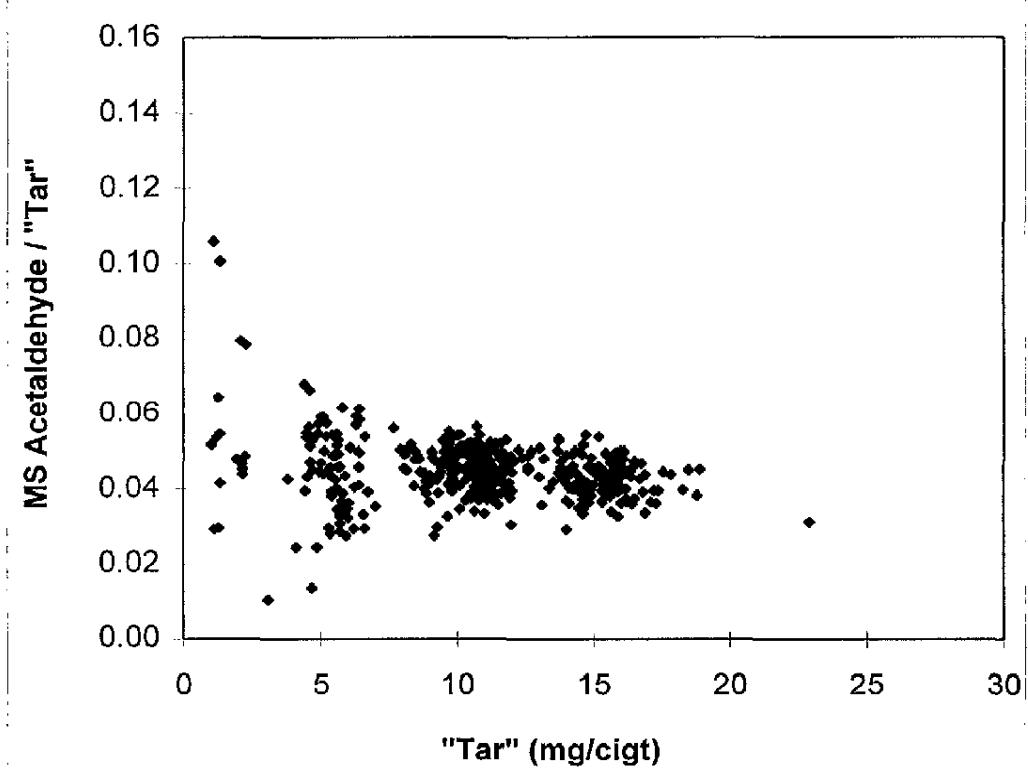


Figure 5. Plot of the ratio FTC MS acetaldehyde/"tar" vs. "tar" for 1992 ($n = 422$).

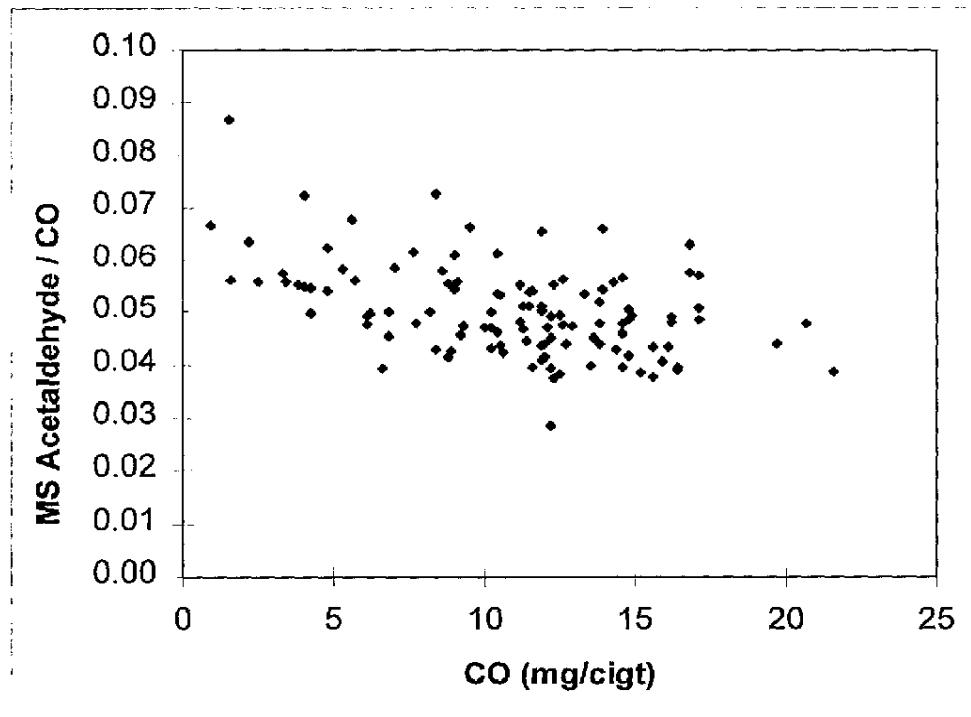


Figure 6. Plot of the ratio FTC MS smoke acetaldehyde/CO vs. CO for 1985 ($n = 116$).

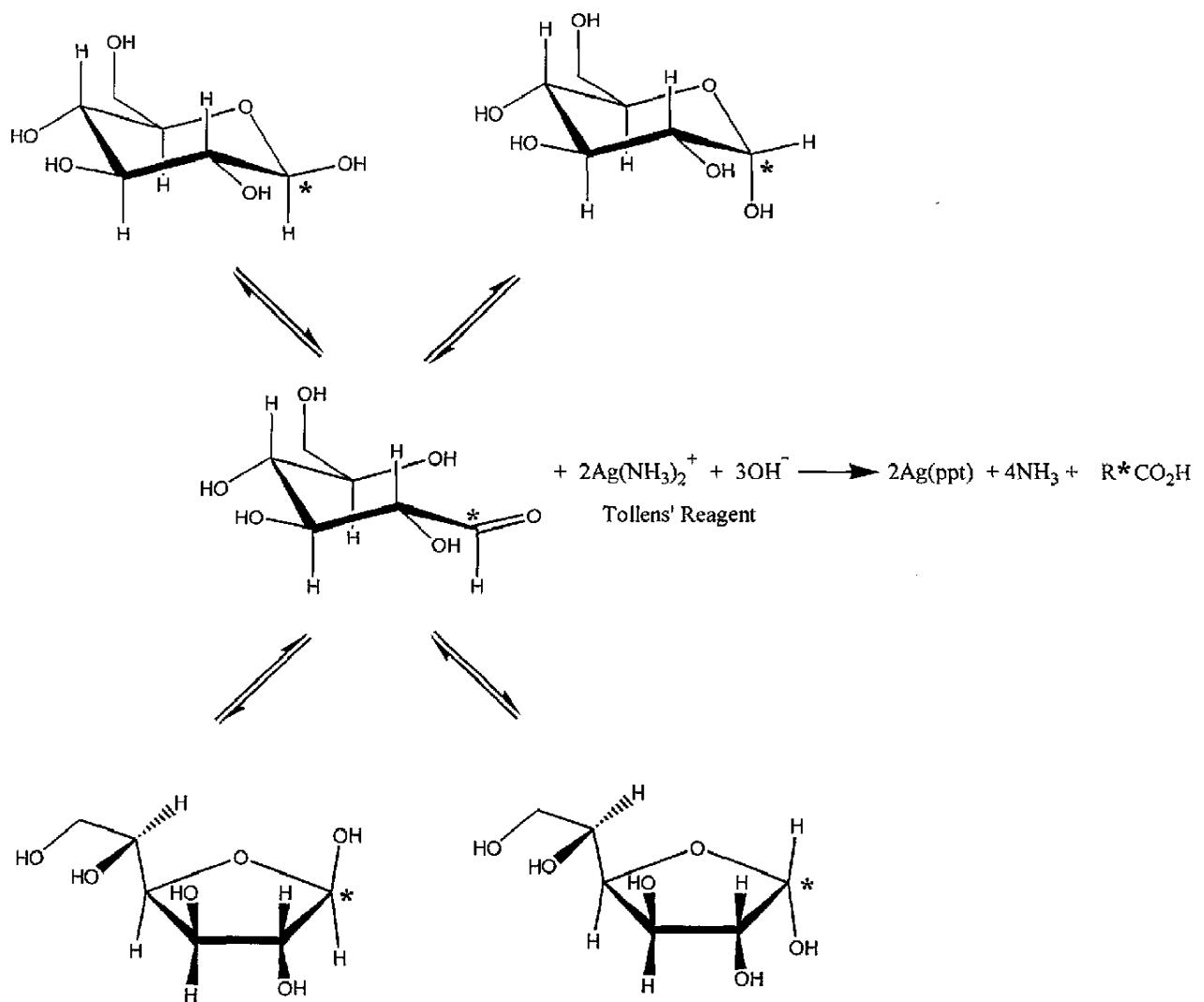


Figure 7. Illustration of the oxidative reactivity of reducing sugars, using D-glucose as the model system.. The anomeric carbon (the *C in the figure) is an aldehyde in the open chain form. The analytical method uses the Tollens' test. Aldehydes can be oxidized by Tollens' reagent to a carboxylic acid. Silver ion is converted to free silver metal.

**Total Reducing Sugars for Brands Tested
1985 - 1993**

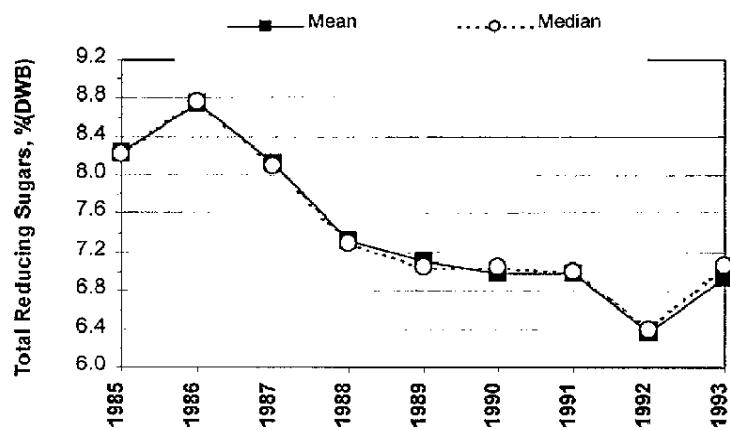


Figure 8. Plot of percent total reducing sugars (dry weight basis) for 1975 through 1993.
For the number of samples, see Table 11.

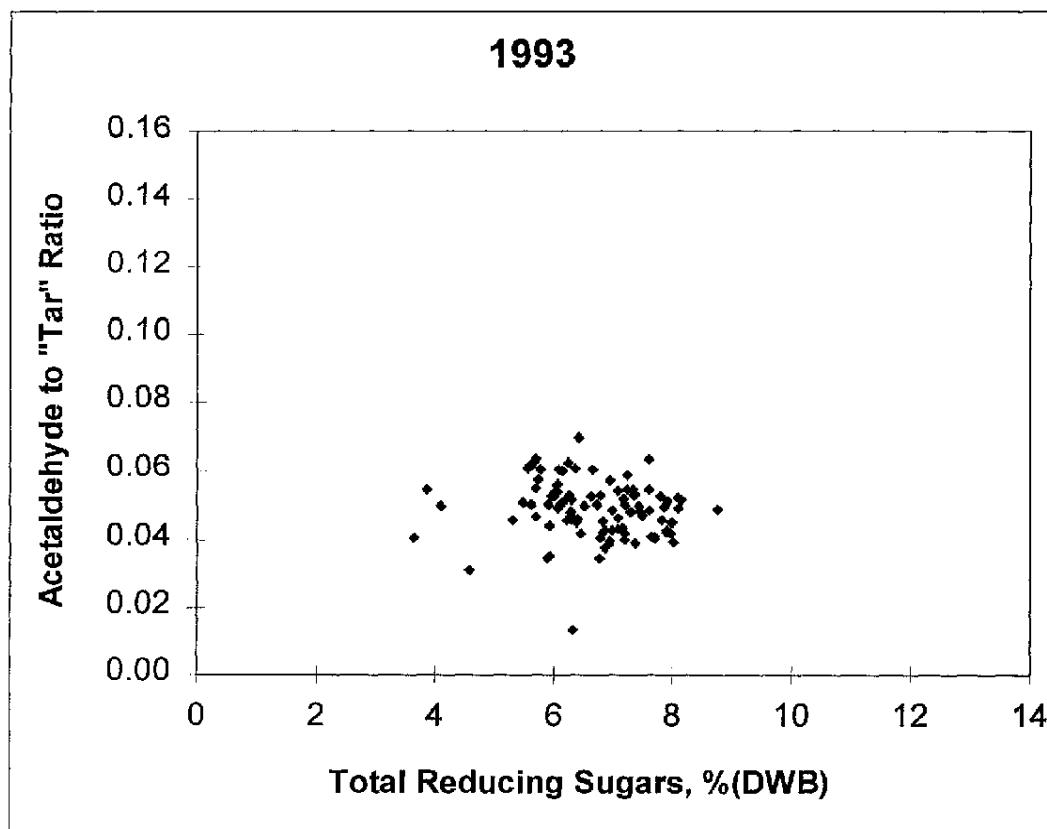


Figure 9. Plot of the ratio FTC MS smoke acetaldehyde/"tar" vs. total reducing sugars for 1993 (n = 102).

Table 1. Puff profiles used in this work and in literature references.

	Puff volume (mL)	Puff duration (sec)	Interval between puffs (sec)	Ventilation hole blocking (%)
FTC^a	35	2	58	0
Labstat Jan. 30, 1997 Report for Massachusetts – “Average”	45	2	34	50
Labstat Jan. 30, 1997 Report for Massachusetts – “Intense” (or “Heavy”)	60	2	26	100
1999 Massachusetts Benchmark Study^b	45	2	28	50

^a 'Federal Register', Vol. 32, Number 147, August 1, 1967. See also 'Federal Register', Vol. 45, Number 134, July 10, 1980. ^b As stated in the Report: "All were taped to achieve 50 % ventilation hole blocking, conditioned under 72 °F +/- 2 and 60 +/- 2 % relative humidity and puffed under the Massachusetts puffing regime of 45 +/- 0.5 mL puff volume with 2 +/- 0.1 second puff duration once every 30 +/- seconds according to the 1999 Massachusetts Benchmark Study Protocol."

Table 2. Comparison of MS smoke characteristics of nicotine and acetaldehyde.

Smoke Property	Nicotine	Acetaldehyde
Mainstream smoke phase	>99% particulate phase	>95% gas phase
Tobacco → mainstream smoke precursor	Thermal decomposition of nicotine salts of natural tobacco carboxylic acids	Formed from many precursors, primarily from tobacco cellulose, other polysaccharides
Formation mechanism	Evaporative transfer from nicotine in tobacco	Pyrolysis and combustion product
Stability in smoke and during analysis	Stable	Likely to react with ammonia, amino acids, other amines. Can polymerize. Can form hydrate with water.

Table 3. Values of MS smoke "tar" and acetaldehyde in the MS smoke of US commercial cigarettes. Data from the Philip Morris USA Testing Laboratory.

Year	"Tar" (mg/cigarette)			Acetaldehyde (mg/cigarette)			Acetaldehyde/"tar"		
	n ^b	Mean +/- standard deviation	Range	n	Mean +/- standard deviation	Range	n	Mean +/- standard deviation	Range
1985	196	10.6 +/- 4.7	1.1-28.3	135	0.52 +/- 0.21	0.03-0.99	135	0.051 +/- 0.010	0.018-0.087
1986	237	11.2 +/- 4.9	1.1-28.4	142	0.51 +/- 0.20	0.02-0.93	142	0.050 +/- 0.010	0.014-0.083
1987	235	10.5 +/- 4.4	1.1-28.4	185	0.53 +/- 0.21	0.02-0.93	185	0.054 +/- 0.011	0.011-0.099
1988	233	10.8 +/- 4.2	1.2-24.2	179	0.56 +/- 0.20	0.07-0.97	179	0.056 +/- 0.009	0.028-0.091
1989	265	10.9 +/- 4.1	1.2-23.5	4	— ^c	— ^c	4	— ^b	— ^b
1990	293	11.0 +/- 4.2	1.3-22.9	116	0.59 +/- 0.24	0.08-1.07	116	0.057 +/- 0.012	0.029-0.090
1991	347	11.0 +/- 4.3	1.0-24.7	325	0.45 +/- 0.18	0.01-0.85	325	0.041 +/- 0.008	0.008-0.071
1992	492	10.8 +/- 4.1	1.0-24.6	422	0.47 +/- 0.18	0.03-0.85	422	0.045 +/- 0.008	0.010-0.106
1993	362	10.7 +/- 4.2	0.5-22.6	102	0.54 +/- 0.20	0.01-0.91	102	0.049 +/- 0.008	0.013-0.070

^a Total reducing sugars are not corrected to dry weight basis. ^b"n" is the number of brands. ^c Not calculated due to the small number of brands tested for MS smoke acetaldehyde in 1989.

Table 4. Mean values of MS smoke acetaldehyde and “tar” from US commercial cigarettes. Data from literature reports.

Source of data	Puff profile	“Tar” (mg/cigarette)			Acetaldehyde (mg/cigarette)	
		Number of brands	Mean +/- standard deviation	Range	Mean +/- standard deviation	Range
Labstat, 1997	FTC	8	8.6 +/- 5.0	0.5-16	0.385 +/- 0.226	0.003-0.705
Massachusetts Benchmark Study (1999)	FTC	26	+/-	-	n/d ^a	n/d ^a
Massachusetts Benchmark Study (1999)	MBS	26	+/-	-	1.458 +/- 0.453	0.596 – 2.133
Chepiga, et al. (2000)	FTC	8 ^b	3.3 +/- 0.90	0.7-7.2	0.237 +/- 0.047	0.0961-0.389
Chepiga, et al. (2000)	FTC	11 ^c	9.9 +/- 0.40	8.10-11.6	0.649 +/- 0.045	0.342-0.812
Chepiga, et al. (2000)	FTC	10 ^d	15.4 +/- 0.4	12.9-17.2	0.916 +/- 0.028	0.726-1.071

^a Not determined. ^b Eight brands were selected from an arbitrary “ultra low tar” range. ^c Eleven brands were selected from an arbitrary “full flavor low tar” range. ^d Ten brands were selected from an arbitrary “full flavor tar” range.

Table 5. For data from the Philip Morris database (see Table 3), smoking parameters and regression analysis data for the linear model of MS smoke acetaldehyde vs. "tar"; i.e., using the linear relationship model:

"MS smoke acetaldehyde yield" = slope x ("tar") + intercept

Sample Description		Best fit parameters			
Year	Number of brands	Slope	Intercept	r^2	p
1985	135	0.0451	0.0545	0.832	<0.00001
1986	142	0.0436	0.0615	0.794	<0.00001
1987	185	0.0446	0.0757	0.843	<0.00001
1988	179	0.0448	0.0962	0.836	<0.00001
1989	4	‡	‡	‡	‡
1990	116	0.0512	0.0531	0.826	<0.00001
1991	325	0.0378	0.0311	0.855	<0.00001
1992	422	0.0409	0.0344	0.870	<0.00001
1993	102	0.0460	0.0329	0.842	<0.00001

‡ Not determined due to small sample size.

Table 6. Smoking parameters and regression analysis data for MS smoke acetaldehyde vs. "tar". Correlations are from literature reports (see Table 4).

Sample Description		Best fit parameters for correlation with MS smoke acetaldehyde						
Source of data	Number of brands	MS smoke parameter	Puff profile	Ax ²	Bx	C (intercept)	r ²	p
Massachusetts Benchmark Study	26	"tar"	MBS	-1.2808	94.978	79.124	0.8209	n/r
Massachusetts Benchmark Study	26	CO	MBS	-2.2875	163.83	-930.76	0.9257	n/r
Chepiga, et al.	25	"tar"	FTC	^a	n/r ^b	n/r	0.91	n/r

^a In the Chepiga, et al. study, the authors used a linear regression model, i.e., A = 0. ^bNot reported.

Table 7. Correlation coefficients for linear relationships between various MS smoke constituents, using Labstat data for the Commonwealth of Massachusetts. The different puff profiles are described in Table 1.

	acetaldehyde (FTC)	“tar” (FTC)	“tar” (average)	“tar” (intense)	CO (FTC)	CO (average)
acetaldehyde (FTC)	1					
“tar” (FTC)	(0.962)	1				
“tar” (average)	0.988 (0.975)	(0.964)	1			
“tar” (intense)	0.969 (0.932)	(0.948)	0.991 (0.984)	1		
CO (FTC)	(0.968)	(0.947)	(0.967)	(0.968)	1	
CO (average)	0.947 (0.936)	(0.878)	0.963 (0.963)	0.965 (0.958)	(0.933)	1
CO Intense	0.862 (0.771)	(0.804)	0.899 (0.862)	0.925 (0.913)	(0.853)	0.950 (0.910)

Numbers in () using eight brands. All others using ten brands.

Table 8. Values of MS smoke “tar” and carbon monoxide in the MS smoke of US commercial cigarettes. Data are from the Philip Morris USA Testing Laboratory.

	MS carbon monoxide (mg/cigarette)			Acetaldehyde (mg/cigarette)		Acetaldehyde/MS carbon monoxide	
Year	Number of brands	Mean +/- standard deviation	Range	Mean +/- standard deviation	Range	Mean +/- standard deviation	Range
1985	116	10.8 +/- 4.3	0.12-1.62	0.53 +/- 0.21	0.06-1.06	0.051 +/- 0.009	0.029-0.087
1993	117	10.8 +/- 4.0	0.90-18.3	0.53 +/- 0.20	0.01-0.91	0.048 +/- 0.006	0.014-0.059

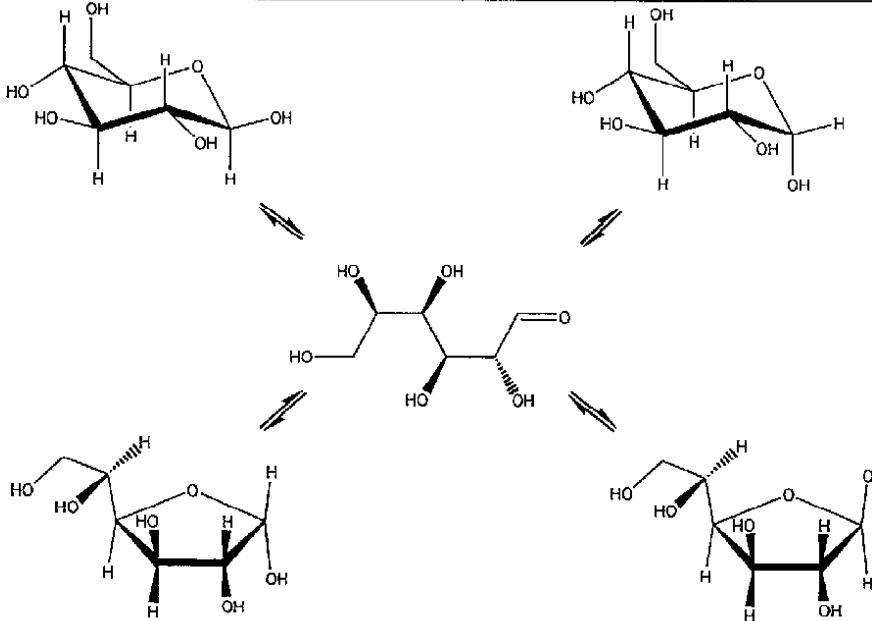
^a “n” is the number of brands.

Table 9. For data from the Philip Morris database (see Table 8), smoking parameters and regression analysis data for the linear model of MS smoke acetaldehyde vs. MS carbon monoxide; i.e., using the linear relationship model:

“MS smoke acetaldehyde yield” = slope x (MS carbon monoxide) + intercept

Sample Description		Best fit parameters			
Year	Number of brands	Slope	Intercept	r^2	p
1985	116	0.0435	0.0590	0.833	<0.00001
1993	117	0.0491	-0.0015	0.934	<0.00001

Table 10. Reducing sugars typically used as additives to tobacco blends.^a

Substance	Structure ^{b,c}
D-Glucose Corn sugar Corn syrup Dextrose	 <p>The table displays five chemical structures of D-Glucose:</p> <ul style="list-style-type: none"> Two chair conformations of D-Glucose, showing axial and equatorial hydroxyl groups. A Fischer projection of D-Glucose, showing the sequence of substituents along the chain. Two Haworth projections of D-Glucose, showing the cyclic form of the molecule.

Maltose	<p>The diagram illustrates the hydrolysis of Maltose. On the left, the structure of Maltose is shown as two D-glucopyranose units linked by a beta(1-4) glycosidic bond. An arrow points from Maltose to its hydrolytic products: D-glucose and D-fructose. The D-glucose molecule is shown with its characteristic alpha anomeric form, while the D-fructose molecule is shown in its cyclic hemiacetal form.</p>
Invert sugar (Obtained by hydrolysis of sucrose.)	<p>A mixture of ca. 50% D-glucose and 50% D-fructose (a non-reducing sugar)</p>

Invert sugar (Obtained by hydrolysis of sucrose.)	A mixture of ca. 50% D-glucose and 50% D-fructose
Honey	Contains 70-80% D-glucose and fructose; 2-10% sucrose (a non-reducing sugar) ^d
Carob bean	Contains usually ca. 40-50% sucrose, D-fructose, maltose and D-glucose, among others ^d
Licorice	Contains a 3-4% mixture of D-glucose and sucrose ^d

^a D-Fructose and sucrose, also added as casings in cigarette manufacture, are not reducing sugars and will not be quantified by the Tollens' reagent test. ^b In some cases, multiple isomers can represent the substance. The actual composition in the tobacco matrix will depend on various matrix conditions, e.g., water concentration, relative concentration of acids and bases and other substances, and temperature. ^c Not all structural isomers illustrated. ^d

Data from: Leung, A. Y.; Foster, S. *Encyclopedia of Common Natural Ingredients*; John Wiley: New York, 1996.

Table 11. Total reducing sugars in blends of commercial cigarettes and correlations with MS smoke acetaldehyde and the ratio acetaldehyde/"tar".

Year	Reducing sugars (% in tobacco) ^a			Correlations of reducing sugars with:		
	Number of brands	Mean +/- standard deviation	Range	Number of brands	Acetaldehyde	Acetaldehyde/ "tar"
1985	162	8.2 +/-1.2	5.3-11.4	135	0.0899	0.0000
1986	187	8.7 +/-1.0	5.7-12.1	142	0.0715	0.0000
1987	193	8.1 +/-0.9	5.9-11.4	185	0.0872	0.0004
1988	182	7.3 +/-0.7	5.7-9.2	176	0.2349	0.0074
1989	210	7.1 +/-0.9	4.9-10.0	4	^a	^a
1990	236	7.0 +/-0.9	4.6-9.4	116	0.1633	0.0206
1991	281	7.0 +/-0.8	4.7-9.2	264	0.1387	0.0004
1992	420	6.4 +/-0.8	4.0-9.4	420	0.0847	0.0541
1993	243	6.9 +/-1.0	3.6-9.4	102	0.0436	0.0209

^a Not determined due to small size of sample.

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